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OPTICAL DIAGNOSTIC SYSTEM FOR THE MEASUREMENT OF GAS TEMPERATURE AND SPECIES CONCENTRATION

P.M. HUGHES AND T. PARAMESWARAN

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OPTICAL DIAGNOSTIC SYSTEM FOR THE MEASUREMENT OF GAS TEMPERATURE AND SPECIES CONCENTRATION

P.M. Hughes* and T. Parameswaran**

ABSTRACT

A technique termed "coherent, anti-Stokes Raman spectroscopy" (CARS) has been developed at the Combustion and Carbonization Research Laboratory of CANMET's Energy Research Laboratories for the measurement of temperature and species concentration. The advantages of this technique over conventional probing methods are improved temporal and spatial resolution; it is nonintrusive and turbulence parameters can be determined. This report discusses the theoretical basis for such a technique and some of the practical considerations involved in the optical arrangement. To apply this technique successfully, it was necessary to develop sophisticated software and hardware. The incorporation of these and the optics into a CARS system is discussed, together with the theory of its application.

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SYSTÈME DE DIAGNOSTIC OPTIQUE POUR MESURER LA TEMPÉRATURE DES GAZ ET LA CONCENTRATION SPÉCIFIQUE

P.M. Hugues* et T. Parameswaran**

RÉSUMÉ

Une technique qui porte le nom de "Coherent Anti-stokes Raman Spectroscopy" (CARS) (Spectroscopie Raman cohérente anti-stokes) a été mise au point au Laboratoire de recherche sur la combustion et la carbonisation des Laboratoires de recherche sur l'énergie du CANMET, pour mesurer la température et la concentration spécifique. L'un des avantages que possède cette technique par rapport aux méthodes classiques d'échantillonnage est une résolution spatiale et temporelle améliorée; la technique est aussi non intrusive et les paramètres de la turbulence peuvent être déterminés. La théorie sur laquelle est basée une telle technique et quelques-unes des considérations pratiques du dispositif optique sont examinées dans le présent rapport. Afin d'appliquer cette technique avec succès, il a fallu développer un logiciel et un matériel mécanographiques perfectionnés. Leur incorporation et celle des appareils optiques dans le système CARS est également étudiée dans le rapport ainsi que la théorie permettant d'appliquer cette technique.

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INTRODUCTION

With the advent of high-energy, coherent light sources such as the laser, a new tool was made available to investigators studying gaseous flow fields. Using the laser, it is possible to make scattering and absorption spectrographic measurements in a gas with high, spatial and temporal resolution. Many techniques have been described, using a multitude of energy-level diagrams, for the determination of gas temperature or species concentration in a gas mixture using laser techniques. A more detailed description of these techniques is given elsewhere (1,2,3,4).

This report deals with a specific technique termed "coherent, anti-Stokes Raman spectroscopy" (CARS). CARS has been found to have better spatial and temporal resolution than other non-intrusive techniques (5,6,7). CARS involves the co-focussing of two laser beams at a point in the test section (Fig. 1). At the point of intersection, a three-photon interaction involving two photons at the pump frequency and one at the Stokes frequency produces a coherent beam at the anti-Stokes frequency. The anti-Stokes frequency is dependent on both the Stokes and pump frequencies. The laser fields interact through the third-order, non-linear susceptibility of the species under study to induce a polarization that generates a radiation at the CARS frequency. This radiation emerges from the test section as a tight, laser-like beam, and, therefore, it is possible to collect all of the generated signal. Because the collected signal is on the anti-Stokes side of the pump frequency, it is free from interferences caused by fluorescence. As a result, the signal-to-noise ratio for CARS experiments is much better than that for other available scattering techniques.

Conventional techniques used for measuring temperature and species concentration require that a probe be immersed to the test point in the measurement field. They are, therefore, termed intrusive techniques. Either a sample of the reacting mixture at the test point is extracted for analysis, or the influence of the gases on the probe tip is monitored. The very presence of the probe in the measurement field causes a distortion of the flow field which influences the mixing processes. In a reacting flow, this distortion may result in changes in the chemical composition and temperature in the vicinity

of the probe. Intrusive techniques require that the probe be protected with a coolant jacket and, as a result, heat is extracted from the flame, which further distorts the temperature field. These disturbances to the temperature and velocity fields and to the mixing processes can result in significant errors in measurement. These errors, coupled with those inherent in the measurement technique, can result in significant differences between the measured and the actual values (8,9). Furthermore, as a result of limitations of the intrusive measurement technique, the measured values are usually limited to time-averaged quantities.

Mention should be made of a few of the classical, optical techniques for measuring temperature and species concentration. The line-reversal technique was first used for measuring flame temperature by Kurlbaum in 1902 (10). Minor modifications have been made to the methodology to include state-of-the-art equipment; however, the basic technique is unchanged. Line-reversal methods use line of sight optics and, as such, only the average temperature along a line through the flame is measured. Furthermore, because of the way in which the measurement is taken, these techniques have poor temporal resolution and cannot be used in turbulent flames. The various Raman scattering techniques are prone to the same problem (1,3,11). A pulsed laser performs the measurements so that a short time resolution is possible; however, the measured signal is incoherent and is generated along the full length of the laser beam in the test section. Using this technique the spatial resolution can only be improved at the expense of the signal-to-noise ratio.

The CARS technique offers an improvement over the intrusive and the classical optical methods. If the power density in the lasers used in CARS experiments is kept below the level for gas breakdown, then the technique is non-intrusive. Because of the coherent nature of lasers, a spatial resolution in the order of 1.0 mm by 100.0 μm is easily attainable. Also, because the measured beam emerges as a collimated, laser-like beam all the generated signal can be collected, which thus improves the signal-to-noise ratio. If the wavelengths of the two laser beams are judiciously chosen, the measured signal can be resonantly enhanced. These and other improvements to the CARS set-up result in a millionfold improvement in the efficiency of signal generation compared with that found in Raman scattering experiments. The lasers used to make CARS

measurements are pulsed and Q-switched and, as a result, a temporal resolution of the order of 10.0 ns is quite common.

The repeated, instantaneous measurement of temperature or composition at a point in the flame allows data to accumulate for the determination of the statistics of the measurements at that point. This kind of information would be useful for the validation of computer models of the test section under study. These models can calculate the distribution of any variable in the test section. It is now generally accepted that the ability to compute parameters in the test section has surpassed the ability to measure them. The availability of dependable data for the validation of computer models has been sadly lacking. Furthermore, information such as Reynolds shears and stresses in turbulent flow have not been available with existing intrusive probes. With the advent of optical diagnostics, the situation has reversed and reliable data, along with turbulent statistics, are now available for the validation of computer models.

This report discusses the practical aspects of a CARS set-up for the measurement of gas temperature and species concentration. The details of the CARS technique and of the theory are discussed elsewhere (1-6). The following describes the CARS measurement system that has been designed and developed at the Combustion and Carbonization Research Laboratory (CCRL). The system involves the integration of two lasers, state-of-the-art optics and detection equipment, and sophisticated software for a dedicated, mainframe computer.

SOURCE-SIDE OPTICS

The optical arrangement for the CARS system is shown in Figure 2. The heart of the CARS system is the neodymium-yttrium aluminum garnet (Nd-YAG) laser. This laser provides the excitation for the dye-laser oscillator and amplifier and provides the pump photons for the CARS interaction. The Nd-YAG laser is pumped by ultraviolet flash lamps oscillating at a rate of 10 flashes per second. The optical cavity is an unstable resonator and, as such, the Nd-YAG beam has a doughnut-like spatial profile. Because the cavity is Q-switch dumped, the laser pulses have a temporal profile from 8 to 10 ns in duration. The Nd-YAG laser produces a beam of light at a wavelength of 1.06 μm. The

output of the Nd-YAG laser is frequency doubled to take advantage of the quadratic dependence of the CARS generation efficiency on the pump frequency and of the optimum, dye-laser pumping efficiency at the doubled frequency.

All the 1.06-μm laser energy leaving the N-YAG laser is not doubled, therefore, the 532.0-nm laser energy is split off from the residual 1.06-μm energy by a harmonic beam splitter (HBS) (see Fig. 2). The residual 1.06-μm laser beam, after being separated from the main laser beam, is directed through a half-wave plate ($\lambda/2$) to ensure that the polarization of the beam is horizontal on entering the second doubling crystal (HD). The beam frequency is redoubled and any residual 1.06-μm energy is absorbed in the KG-3 filter. The redoubled laser beam is then used to pump the dye oscillator. The lens arrangement in the dye-laser pump beam (see Fig. 2) reduces the beam to the appropriate size. The dye cell (DC) is maintained at Brewster's angle to ensure that the dye-laser beam is horizontally polarized. The interference filter (TF) in the dye-laser oscillator cavity is a tuning filter used to shift the dye-laser spectral profile so that the spectral envelope covers the necessary Stokes wavelengths.

The originally doubled, Nd-YAG (2 x Nd-YAG) laser beam at 532.0 nm is directed through a KG-3 filter to remove any 1.06-μm energy. Part of this laser beam is used to excite the dye in the dye-laser amplifier. Usually about 30% is used for dye pumping and the residual 70% is directed to the CARS test section. The dye amplifier cell (DC) is at Brewster's angle to maintain the horizontal polarization of the dye-laser beam.

The laser beams are then combined to produce the CARS signal. A variety of configurations exist for this combination. Details on the various CARS geometries are given elsewhere (7). The different configurations result from the various attempts to ensure that phase-matching conditions are met at the CARS test point. For the experiments at CCRL, a quasi co-linear CARS arrangement is employed. The dye and 2 x Nd-YAG beams are combined after they have been sized to fit together. The dye beam is made to travel along with the 2 x Nd-YAG beam through the hole in the 2 x Nd-YAG beam doughnut profile by means of the beam-combining filter (D). These beams are then focussed through

a lens (L) before entering the test section (TS). In the region of the focal spot the two beams intersect and, through an interaction with the molecule under study, the CARS signal is generated.

The CARS beam, which emerges with the dye and 2 x Nd-YAG beams, is a coherent beam located in an annular region about the dye-laser beam (Fig. 3). The location of the CARS beam is dependent on the physical characteristics and wavelengths of the probe beams (12-14). The interaction length depends on the focal length of the focussing lens and the diameter of the beams entering the lens. To study the CARS beams, the dye and 2 x Nd-YAG beams must be removed, which is done by using interference filters (F) that pass only the CARS wavelengths. Before the CARS beam enters the spectrometer, part of the beam is split off and sent to a photomultiplier tube (PMT). This aids in "tweaking" the probe beams to ensure optimum overlap in the test section.

The output of the PMT is sent to a "boxcar" averager where the average of a number of CARS signal pulses is displayed. This monitors the CARS signal strength while adjustments are made to the mirrors directing the probe beams. Optimization of the CARS signal is necessary because of the quadratic dependence of the CARS signal strength on both the pump beam intensity and the number density of the probe molecule. Minor fluctuations in either one result in a large variation in the CARS signal. The "boxcar" averager smooths out variations caused by extraneous sources and allows the operator to follow trends as adjustments are made to the position of the two probe beams. Once the CARS sample geometry has been optimized, the CARS signal is ready to be analysed in the holographic grating spectrometer (HGS).

The CARS signal is carried to the HGS by means of a fibre optic. The fibre has an 80-μm core, a 125-μm cladding, and is made of fused silica. After removing the probe beams from the beam leaving the test section, a lens (L) (see Fig. 2) focusses the CARS beam onto the input end of the fibre optic. The fibre then carries the optical signal to the HGS for analysis. This fibre-optic link allows for the separation of the source-side optics from the detection-side optics. The detection and study of the CARS signal can then be carried out in an area remote from the combustion environment.

DETECTION-SIDE OPTICS

As with the dye laser, the HGS was designed specifically for the CARS experiment. The layout of the spectrometer is shown in Figure 4. The entire spectrometer is enclosed to eliminate extraneous illumination. The CARS signal is brought into the spectrometer by means of the fibre optic (FO) (see Fig. 4). The 80-μm core diameter acts as the entrance slit to the spectrometer. The light, on leaving the fibre, is directed to the holographic grating (HG) by means of a 45° prism (P). The fibre has a numerical aperture of about 0.20 and, as such, overfills the grating. The specifications of the grating are given in Table 1. After the CARS beam is dispersed by the grating it is directed to the detector head. The detection of the dispersed CARS signal is done by means of an intensified diode array (see OMD, Fig. 4). The array is 1 x 25 mm. Along the long axis of the array are placed 1024 diodes 1 mm high. The dispersion plane of the grating is made parallel to the long axis of the detector so that the dispersed signal can be broken into 1024 elements. The grating is constructed so that the image of the 80-μm tip of the fibre through the grating is an oblong spot about 1.5 mm high and 25 mm long. The input and output beams for the grating are arranged one above the other to conserve space (see Fig. 4) with the detector placed just behind and above the prism. The intensifier is an integral part of the detector and is placed just in front of the detector diodes. The CARS signal can be quite weak, and, after passing through the various optics, may be even weaker when it reaches the detector. The intensifier can amplify the optical signal by as much as 4000 times. The intensifier is also gated and as such the signal-to-noise ratio can be improved by gating the intensifier to operate only when the laser is flashing. Thus, only photons that are generated through the CARS interaction are amplified for the detector.

Successful measurement of CARS spectral profiles is dependent on synchronization of the source-side optics with the detection-side optics. Synchronization is achieved by a controller that determines the rate at which the laser will

flash and when the detector will read the detected signal. The controller also controls the gate on the intensifier.

MEASUREMENT TECHNIQUE

To determine the temperature at a point in the test section, the CARS spectral profile is recorded and is then compared with a theoretically calculated spectral profile. Any molecule in the test section can be used to determine the temperature; however, nitrogen is commonly used for various reasons. The spectrographic and line-width parameters for nitrogen are well known. Furthermore, the strength of the CARS signal varies as the square of the number dersity of the probe molecule. Nitrogen is used for measuring temperature because it is in abundant supply in air-breathing combustion. It has been found that the CARS spectral profile is relatively insensitive to the concentration of the nitrogen molecule above 50% (7). The spectral profile is, however, quite sensitive to changes in temperature. This sensitivity can be seen in the calculated CARS spectral profiles for nitrogen (Fig. 5) for temperatures ranging from 1200° to 2400°K. These curves correspond to the Q-branched vibrational transitions of the nitrogen molecule for a CARS interaction.

The calibration measurements that must be made before a temperature can be determined from the CARS spectral profile can be divided into two basic groups: variable and long-term. The long-term calibration measurements consist of the slit function and the dispersion of the spectrometer and the spectral profile characteristics of the pump laser. The slit function of the spectrometer is the response of the spectrometer to monochromatic irradiation. It can be thought of as the broadening of the spectral profile because of the finite width of the entrance slits. The long-term calibration values have been shown not to change over time. A recalibration is usually performed when changes are made to the optics involved. The variable calibration parameters involve the measurement of the dye-laser spectral profile and the determination of the diode wavelength relationship for the detector. These parameters have been shown to change from day to day. Therefore, they form part of the series of measurements taken before each experiment.

The dispersion of the spectrometer is measured by illuminating the entrance slits with calibration lamps having elemental electrodes. The emission lines of these elements are well known and are published in the literature (15). Using the diode location of these emission lines and corresponding wavelengths, a functional relationship between diode number and wavelength can be determined.

To determine the slit function of the spectrometer, a nitrogen CARS spectrum is generated at room temperature and is carried into the spectrometer by the optic fibre. The functional form of the slit function is determined by curve-fitting techniques. A range of functions can be used to describe the slit function of the spectrometer including triangular, exponential, and Gaussian functions. The pump-laser is run in a single mode. Therefore, the line width of the pump-laser beam is less than 0.02 cm^{-1}, which will result in a minimum of error in assuming that the pump laser is truly monochromatic. The mathematics would become intractable if the susceptibility were to be convolved with the pump laser as well as with the dye-laser. There is, however, some loss in CARS signal strength if the pump laser is run single mode.

In a multiplex CARS system a broad-band dye laser is used so that the entire CARS spectrum can be generated in a single shot. The dye profile can be monitored by splitting off a portion of the dye beam and sending it to be dispersed and studied, which requires that a separate monochromator be maintained for the dye-laser wavelengths. A more economical way is to place a calibration cell in the CARS experiment filled with a gas, the resonant susceptibility of which is spectrally far removed from that of the probe molecule. When the CARS lasers intersect in the reference gas, a non-resonant signal is generated and the shape of the spectral profile of the dye laser is reflected in the non-resonant signal generated. This technique is generally accepted for determination of the dye-laser spectral profile because it also gives an indication of the distortion of the CARS signals resulting from all optics in the complete optical arrangement.

When the short-term calibration has been completed, the measurement of the flame temperature with the laser beams is possible. The laser beams are directed into the test section to the sample point. Depending on the type of

measurement being performed, the laser beams are scanned throughout the test section to collect many single-point CARS spectra or left at one test point for a multi-shot average spectrum. As the spectra are collected, they are sent to the computer for analysis. The analysis involves the manipulation of large, vector arrays and these computations cannot be carried out in the time between the firing of the laser (0.1 s). Therefore, the CARS spectra, along with the short-term calibration spectra, are stored on hard disc for future analysis.

The determination of species concentration in a flame is carried out somewhat similarly; however, a different dye laser would be chosen to satisfy the resonant enhancement condition. Different software would be used to calculate the "best fit" spectral profile, and the concentration of the species under question.

DATA TRANSMISSION

The computer used for data reduction and storage of the spectra is located in an area remote from the optical set-up and, as such, it is necessary to send large blocks of data over long distances. These data can be transmitted in a serial or parallel fashion. Serial transmission of spectra is slow (about 0.3 spectra per second); however, it allows the operator to discriminate between good and bad spectra as they are collected. Parallel transmission is fast (10 spectra per second) but the data, good or bad, are transmitted to the computer for analysis.

Specialized software has been developed for the mainframe computer for serial transmission. Programs are menu driven and allow the operator to log onto the mainframe computer, to open storage files, and to send data from the detection equipment to the computer without leaving the optical equipment. Thus, the mainframe computer handles the detection equipment as if it were another terminal. The physical link between the computer and the detection equipment consists of 90 m of six-twisted-pair cable and a short-haul modem at each end.

Parallel transmission is handled somewhat differently. Before starting, the operator uses the same serial link to the computer to run menu-driven software in preparation for the experiment. After preparation, a program is run that tells the computer to communicate with the detection equipment and to store the spectra as they are collected. The detection equipment in this case is handled by the mainframe computer as if it were a peripheral device. The physical link to the computer consists of two specially designed long-line drivers and 90 m of 10-twisted-pair cable.

FILE MANAGEMENT SYSTEM

To collect and analyze large amounts of data, a comprehensive file management system is necessary. The system used for the CARS experiments takes into account the various types of experiments conducted and the different data formats required by the analysis programs. The file management software is divided into two types: one each for the serial and parallel data transmission methods.

SERIAL DATA FILES

The serial data transmission software is used when special spectra are to be collected, e.g., dye-laser spectral profiles, and when data collection and transmission speeds are unimportant.

When the experimental arrangement is ready, the operator runs the appropriate program. The program runs in a question-and-answer mode. By responding to the questions, the operator first creates a description file that describes the experiment to be conducted. This file describes the group of data files that will make up the data series collected for the experiment. The program also creates automatically a header file that describes the records contained in a data file. When the description and header files are completed, the program awaits the signal to accept the data. Data are sent from the mainframe controller for the optical multichannel detector (OMD) (see Fig. 4). The operator either selects the spectral data memory location of the data file to be sent or acquires the data file manually. By depressing the output

button on the controller, the spectrum that is currently being displayed, is transmitted to the computer. For a complete spectrum of 1024 points this transmission takes about 30 s. Therefore, this type of data transmission cannot be undertaken in real time. At the end of the data transmission, the program stops and to transmit additional spectra the operator must initiate the transmission software again. Thus, the operator indicates which description file refers to the data file to be collected and creates a new header file describing the data file. The operator continues in this mannner until all the spectra are transmitted.

PARALLEL DATA FILES

Parallel data transmission software is used for the rapid acquisition and storage of large amounts of spectral data. The file management system automatically organizes the data file into calibration spectra and data spectra so that the maximum speed (10 spectra per second) is used during data collection.

As with the serial program, the parallel program creates the necessary descriptive and header files and allows the operator to choose the type of experiment to follow. The data file is organized appropriately depending on the type of experiment. The first record of the data file for an experiment consists of information indicating the type of data that follow and the location of special reference spectra. These special spectra make up the short-term calibration spectra and are collected and stored as the second and third records of the data file indicated in the reference record. The next record may be blank or may consist of an average hot spectrum depending on the type of experiment. As many as five special records may be stored at the beginning of a data file. Successive records are usually single-shot spectra. Each file consists either of average and single-shot spectra at a single point in a flame, or of measurements along a specified line through the flame. As such, each file is given a unique file name and a header, which describes the conditions under which the data were collected.

Significantly, data that are collected using parallel-transmission software are collected in real time. Thus, the data acquisition, transmission, and storage is done in less than 0.1 s. Large data files can be built using the

parallel-transmission software whereas data files collected using the serial-transmission software are usually smaller and contain special data. Special data are handled individually and differently from those collected using the parallel-transmission data files. The parallel-transmission software is the "work horse" for the CARS experiment. Data files created using this software consist of measurements mapping an entire flame and each record is handled similarly. Therefore, software has been created to reduce the data collected using the parallel-transmission software. The data collected using the serial-transmission software are handled individually and will be the subject of another report.

DATA REDUCTION

The theory of coherent, anti-Stokes Raman spectroscopy has been dealt with extensively (16-19). In brief, CARS is a non-linear, optical phenomenon and involves three-wave mixing. When two laser beams of frequencies ω_ℓ and ω_s interact in a medium, three-wave mixing produces a resultant coherent beam with the frequency $2\omega_\ell - \omega_s$ which is the CARS beam (see Fig. 1). The mixing occurs for all samples but the intensity of the CARS signal is greatly enhanced when $\omega_\ell - \omega_s$ approaches a Raman frequency of the medium.

The interaction of laser radiation with the medium occurs through the third-order, non-linear, electric susceptibility denoted by $\chi^{(3)}$ and gives rise to an induced polarization field, which acts as a source term in Maxwell's wave equation. On solving the wave equation, one arrives at the following expression for the power of the CARS signal:

$$P_3 \propto P_\ell^2 P_s \left| \chi^{(3)} \right|^2 \qquad \text{Eq 1}$$

The CARS power P_3 varies linearly with the Stokes power P_s, quadratically with the pump power P_ℓ and is also proportional to the square of the third-order susceptibility. $\chi^{(3)}$ has resonant and non-resonant contributions:

$$\chi^{(3)} = \chi^{R} + \chi^{NR}. \qquad \text{Eq 2}$$

The non-resonant component χ^{NR} is independent of frequency and varies linearly with number density.

If the Raman lines can be considered to be narrow enough to avoid any overlap, the resonant component χ^{R} can be expressed as:

$$\chi^{R} = \frac{hNc^{4}}{\pi\omega_{s}^{4}} \left|\frac{d\sigma}{d\Omega}\right|_{j} \left(\frac{\Delta_{j}\,\omega_{j}}{\omega_{j}^{2} - (\omega_{\ell} - \omega_{s})^{2} - i\,\Gamma_{j}\,(\omega_{\ell} - \omega_{s})}\right) \qquad \text{Eq 3}$$

where: N is the number density, ω_{j} is the Raman frequency, Δ_{j} is the population difference between the upper and lower vibration-rotation states for the transition, Γ_{j} is the Raman line width, and $d\sigma/d\Omega$ is the Raman-scattering cross section (20).

It is clear that χ^{R} becomes large when:

$$\omega_{j} = \omega_{\ell} - \omega_{s}. \qquad \text{Eq 4}$$

If we define the frequency detuning as

$$\Delta\omega = \omega_{j} - (\omega_{\ell} - \omega_{s}) \text{ and if } \Delta\omega/\omega_{j} \ll 1 \qquad \text{Eq 5}$$

$$\frac{1}{\omega_{j} - \Delta\omega} = \frac{1}{\omega_{j}}\left(1 + \frac{\Delta\omega}{\omega_{j}}\right) \qquad \text{Eq 6}$$

then Equation 3 becomes:

$$\chi^{R} = \frac{hNc^{4}}{\pi\omega_{s}^{4}} \left|\frac{d\sigma}{d\Omega}\right|_{j} \left(\frac{\Delta_{j}}{2\Delta\omega_{j} - i\Gamma_{j}}\right) \qquad \text{Eq 7}$$

and let $K_{j} = \frac{hNc^{4}}{\pi\omega_{s}^{4}} \Delta_{j} \left|\frac{d\sigma}{d\Omega}\right|_{j} \Gamma_{j}^{-1}.$ Eq 8

Summing overall such ω_j where j refers to the vibrational and rotational quantum numbers then:

$$\chi^{(3)} = \sum_j \frac{K_j \Gamma_j}{2\Delta\omega_j - i\Gamma_j} + \chi^{NR}. \qquad \text{Eq 9}$$

The Raman cross-section $\frac{d\sigma}{d\Omega}$ can be expressed as follows for the Q branch:

$$\left|\frac{d\sigma}{d\Omega}\right|_j = \frac{\omega_s^4}{c^4} \frac{\pi}{hM\omega_o} \left(\alpha^2 + \frac{7}{45} b_j^j \gamma^2 (v+1)\right) \qquad \text{Eq 10}$$

where: M is the reduce mass, ω_o the angular frequency of the molecular oscillator, b_j^j are the Placzek-Teller coefficients, α is the derivative of the mean molecular polarisability with respect to the inter nuclear co-ordinate γ is the similar derivative of anisotropy, and v is the vibrational quantum number of the initial level.

$\chi^{(3)}$ can thus be calculated from Eq 9.

In the above analysis, the pump frequency (ω_ℓ) and the Stokes frequency (ω_s) have been assumed to be ideally monochromatic, which is indeed the case in some experiments. In this case, the Stokes frequency is scanned with each laser flash and the complete CARS spectral profile is generated point by point. This scanning technique results in a rather simplified detection-side optical arrangement because all that is needed is a photomultiplier tube as a detector. In addition, the signal collected tends to be much stronger. There is, however, one drawback to this type of CARS signal generation, which restricts it to limited usage. This limitation involves the time required to generate the complete CARS spectral profile. The completion of the scanning of the CARS spectral profile may take as much as 15 to 20 min. This time then restricts the use of a scanning CARS technique to a situation in which the concentration or temperature field does not change during the scanning period. In turbulent combustion this situation is impractical and so a technique termed "broadband" CARS is used.

Broadband CARS derives its name from the Stokes laser spectral profile. The Stokes laser is designed to have a spectral profile that is broad enough to generate the CARS frequencies in one shot. The advantage of the broadband CARS technique is that the complete anti-Stokes profile is generated with each shot of the lasers. Thus the temperature or concentration measurement is frozen in time. With each shot of the lasers, a history of the fluctuation of the measurement can be stored. With this information, a probability distribution function (PDF) of the measurement can be created. For this reason the broadband technique is used for the measurement of temperature and species concentration in turbulent combustion.

In practice, the pump laser has a finite spectral width as well. In this case the CARS power $P_3(\omega)$ can be obtained by convolving over the laser widths, according to the procedure outlined by Yuratich (21). Then

$$P_3(\omega) = \int P_\ell(\omega_\ell)d\omega_\ell \int P_\ell(\omega - \delta)\, P_s(\omega_\ell - \delta)\, \left|\chi(\delta)\right|^2 d\delta. \qquad \text{Eq 12}$$

Generally, $\Delta\omega_\ell \ll \Delta\omega_s$, and $\Delta\omega_\ell$ is very small. Therefore, $P_s\{\omega_\ell - \delta\}$ can be replaced by $P_s(\omega_\ell^{(0)} - \delta)$ and the integral can be simplified to

$$P_3(\omega) \approx \int P_s(\omega_\ell^{(0)} - \delta)\, P_\ell\{\omega - \delta\}\, \left|\chi(\delta)\right|^2 d\delta \qquad \text{Eq 13}$$

where: $\omega_\ell^{(0)}$ is the centre frequency of the pump laser.

A Gaussian distribution may be assumed for the spectral densities $P_\ell(\omega_\ell)$, $P_s(\omega_s)$

i.e., $$P_\ell(\omega_\ell) = \exp -\left(\frac{\Delta\omega_\ell}{\text{width}}\right)^2 \qquad \text{Eq 14}$$

$$P_s(\omega_s) = \exp -\left(\frac{\Delta\omega_s}{\text{width}}\right)^2 \qquad \text{Eq 15}$$

where: $\Delta\omega_\ell = \omega - \omega_\ell$, $\Delta\omega_s = \omega - \omega_s$
width denotes the full line width at half maximum intensity.

Equation 13 gives the CARS spectral profile as it is generated in the test section. As the CARS signal is carried to the spectrometer, changes to the spectral profile may result from the band-pass characteristics of the optics along the beam path. Furthermore, a convolution is required to include the detector response and the slit function of the spectrometer. When these factors have been included in the spectral profile, the gas temperature or species concentration are ready to be determined.

From Equation 7 it can be seen that the resonant CARS intensity varies with temperature through its dependence on the number density N, population factor Δ_j and Raman line width Γ_j, all of which are functions of temperature. The total CARS intensity also depends on the non-resonant contribution, which in turn varies with species concentration and temperature. These features, then, are the basis of temperature and concentration measurements in CARS spectroscopy.

A computer program based on Equation 13 was provided to CCRL by R.J. Hall and A.C. Eckbreth of United Technologies Research Centre, USA. Subsequently, this program was modified, speeded up, and used to generate theoretical CARS spectra.

Any molecule in the test section can be used to measure the temperature; however, because the CARS signal strength depends quadratically on the number density of the generating molecule, nitrogen is used in air-breathing combustion. In the variation of the theoretical CARS spectrum with temperature (see Fig. 5), two main structures are noteworthy in the spectral profiles. The largest spike at about 21 125 cm^{-1} is termed the "fundamental" peak and corresponds to the v = 0 to v = 1 Q-branch transitions. The second peak is called the "hot band" and results from the v = 1 to v = 2 Q-branch transitions. The fine structure on the spectral profile results from individual Q-branch transitions. As the temperature of the molecule or the resolution of the spectrometer is reduced, this structure becomes smooth.

The effect of varying the concentration of the species under consideration on the CARS spectral profile is shown in Figure 6 (22). Here the CARS spectrum of carbon monoxide (CO) is shown for various concentration levels.

Recently, it was pointed out by Teets (23) that the Yuratich approximation in Equation 13 for the laser width convolution, when multi-mode lasers are used, may lead to errors in temperature and concentration estimates if the laser width is comparable to the Raman-line width. Therefore it is necessary to use single-mode lasers to provide the pump beam, which results in the 0.02 cm^{-1} line width for the pump laser as mentioned earlier.

DATA ANALYSIS

The calculation of the gas concentrations, using the CARS spectral profiles as input, is handled roughly in the same manner as in the calculation of the gas temperature. This similarity is particularly true of the curve-fitting analytical techniques. Consequently, the discussion of the analysis of the data concerns itself with the determination of gas temperatures.

Experimental CARS spectra are recorded as arrays of CARS power values as a function of diode numbers in the diode-array detector. After background subtraction, it is necessary to calibrate the detector to convert the diode scale to wave-number scale. This conversion is done by studying the response of the detector to known sharp lines from a powerful lamp and by calibrating the result with suitable curve fitting. Such a calibration determines the detector dispersion relation to within a constant. This constant is obtained by recording a room-temperature, N_2, CARS spectrum and by assigning the theoretically obtained frequency to its peak. Spectra obtained from the hot medium can be then converted to cm^{-1} scale with the dispersion equation.

In Equation 13, the broad-band Stokes laser has a wide frequency range, as its name implies. Hence, the effect of convolving with its profile is to modify the overall shape of the spectrum. The effect of the dye laser and other unknown system response effects on the resonant CARS spectrum can be eliminated by dividing it with a non-resonant CARS spectrum, after which the theoretical spectrum does not need a dye convolution.

Thus the data-reduction program does the following:

- reads a room-temperature, N_2, CARS spectrum;
- reads a non-resonant CARS spectrum with argon or carbon dioxide;
- finds the peak of the N_2 spectrum in diode number and assigns a theoretical frequency to it;
- uses the dispersion equation to set up the frequency scale;
- reads hot CARS spectra;
- divides it by non-resonant spectrum;
- compares the hot spectra with theory; and
- predicts a temperature.

As already stated, the N_2, Q-branch, CARS spectrum is used for estimating temperatures. The simplest approach to doing this would be to fit the spectrum with theoretical spectra by a least-mean-square procedure. However, the generation of theoretical spectra for each iteration would be time-consuming and expensive. A more efficient scheme of using a table of theoretical, N_2, CARS spectra generated at 50°K intervals is used for the analysis. There is also a routine for interpolation in between the 50°K interval. In this manner, temperature is used as a parameter for fitting the theoretical CARS spectral profile to the experimental profile.

To correct for any frequency shift between the theoretical and experimental CARS spectra, the shift is also used as a fitting parameter in the analysis. The fitting is done by a non-linear, least-mean-square scheme (24).

FAST-FITTING ALGORITHMS

An alternative method of finding temperatures from CARS spectra is to use characteristics of the spectral profiles themselves. Such parameters as the ratio of the peak heights of the fundamental band to the hot band are found to be unique functions of temperature, and, as such, can be used in a fast-fitting scheme (25). This type of scheme is expected to be faster and more efficient than the least-square method described earlier. The improved

speed comes from the fact that it is not necessary to monitor the fit between the experimental and theoretical spectra. Furthermore, by using fast-fitting methods it is not necessary to maintain large data files of theoretical spectra.

Parameters used in the fast-fitting scheme are listed below (Fig. 7):

- area of fundamental band/height of fundamental band (AF/HF Fig. 8);
- peak height of hot band/peak height of fundamental band (HH/HF Fig. 8);
- area of warm section/area of cold section of fundamental band (AW/AC Fig. 8);
- area of hot band/area of cold section of fundamental band (AH/AC Fig. 8); and
- slope of log plot within 12-75% of peak height fundamental band (slope log 12-75%, Fig. 8).

By using the theoretical CARS spectra the variation of these parameters with temperature has been found (see Fig. 8). The information in Figure 8 is tabularized into a table which can then be interpolated linearly to yield the temperature for a given experimental spectrum.

Tests have been conducted comparing the least-mean-square to the fast-fitting data reduction schemes. These tests used synthetic experimental spectra as input derived from a combination of a known set of theoretical and noise spectra. The results of these tests indicate that the fast fitting routines are indeed faster by a factor of 2.

However, the implementation of fast-fitting techniques must await further study of the characteristics of the fitting parameters. Two methods are currently being studied for using the fast-fitting parameters. The first involves a scheme to give a weighted average of the temperatures resulting from the five parameters. The weighting will depend on the temperature range and the sensitivity of the parameter to noise. The other method involves a rating

technique whereby the temperatures resulting from each parameter will be compared with the average of the other temperatures. In this way, temperatures that differ significantly from the average of the others can be eliminated.

DATA DISPLAY

A menu-driven program has been developed whereby experimental data can be viewed at any time during processing. It is also possible to change the long- and short-term calibration spectra used in data reduction. In this way, the effect of non-resonant background can be studied.

This display package was written for comparison of spectra. The spectra to be compared are plotted one on top of the other, which allows the difference between the two spectra to be seen. These two spectra may be a single-shot and a multiple-shot average CARS spectra or experimental and theoretical CARS spectra. To aid in the comparison of the spectra, simple mathematical manipulations of the two spectra, such as B - A, A - B, B ÷ A, and A ÷ B, can also be plotted on the same graph. Thus specific regions of the spectrum can be investigated for poorness of fit or noise.

A sample display is shown in Figure 9, in which a single-shot and average spectra are compared. The lower trace shows the difference (A - B) between these two spectra.

CONCLUSIONS

A complete system has been developed for the non-intrusive measurement of temperature and species concentration in a combusting environment. The technique, termed "coherent, anti-Stokes Raman spectroscopy", uses two high-powered, pulsed lasers to generate the signal to be measured. The signal so generated emerges from the test section as a laser-like beam and, as such, all of the generated signal is captured for analysis. The technique has advantages over current measurement techniques in that the measurement does not disturb the flame and is frozen in time, the sample volume is small, and the quality and type of measurement taken is more useful to the combustion modeller. The CARS technique developed at CCRL uses advanced software and hardware techniques, thus giving a state-of-the-art measurement system.

PLANNED SYSTEM IMPROVEMENTS

Refinements to the optical arrangement, planned to improve the signal-generating efficiency, include realignment of the axis of polarization of the residual 1.06 μm used for pumping the dye-laser oscillator; changing the focal length of the laser-focussing lenses; and readjustment of the partitioning of the doubled YAG laser beam. The first improvement should allow for more efficient pumping of the dye laser and thus more energy in the Stokes beam. The last two refinements should result in a greater amount of energy in the pump beam used in the CARS interaction. More recent developments on CARS theory will be included in the analysis, to get better agreement between theory and experimental results. Implementation of the fast-fitting techniques will also be studied.

REFERENCES

1. Eckbreth, A.C.; Bonczyk, P.A.; and Verdieck, J.F. "Review of laser Raman and fluorescence techniques for practical combustion diagnostics"; United Technologies Report for the EPA Office of Research and Development, *EPA Report No.* EPA-600/7-77-066; June 1977.

2. Eckbreth, A.C.; Bonczyk, P.A.; and Shirley, J.A. "Investigation of saturated laser fluorescence and CARS spectroscopic techniques for combustion diagnostics"; United Technologies Report for the EPA Office of Research and Development, *EPA Report No.* EPA-600/7-78-104; June 1978.

3. Eckbreth, A.C.; Bonczyk, P.A.; and Verdieck, J.F. "Combustion diagnostics by laser Raman and fluorescence techniques"; *Progr in Energy and Combust Sci* 5:253-322; 1979.

4. Eckbreth, A.C. "Use of lasers in nonlinear Raman spectroscopy"; *United Technologies Report No.* UTRC 82-28; May 1982.

5. Eckbreth, A.C. "CARS thermometry in practical combustors"; *Combust and Flame* 39:133-147; 1980.

6. Eckbreth, A.C., and Schreiber, P.W. "Coherent anti-Stokes Raman spectroscopy (CARS): Application to combustion and gas-phase diagnostics"; *Chemical Applications of Nonlinear Raman Spectroscopy in Laser Applications*, Vol 1; Academic Press; 1981.

7. Hall, R.J., and Eckbreth, A.C. "Coherent anti-Stokes Raman spectroscopy (CARS): Application to combustion diagnostics"; *Laser Appl*, Vol 5; Academic Press; 1984.

8. Tine, G. *Gas Sampling and Chemical Analysis in Combustion Processes*; Pergamon Press; 1961.

9. Zinn, B.T., Editor. "Experimental diagnostics in gas phase combustion systems"; *Progr in Astronaut and Aeronaut* 53; 1977.

10. Kurlbaum, F. "A simple method for determining the temperature of luminous flames"; (Translated from German), *Physikalische Zeitschrift* 3:187-188; 1902.

11. Eckbreth, A.C. "Recent advances in laser diagnostics for temperature and species concentration in combustion"; *18th Int Symp on Combust*; 1471-1488; 1981.

12. Marko, K.A., and Rimai, L. "Space and time-resolved coherent anti-Stokes Raman spectroscopy for combustion diagnostics"; *Optic Soc Am* 4:7:211-213; 1979.

13. Davis, L.C.; Marko, K.A.; and Rimai, L. "Angular distribution of coherent Raman emission in degenerate four-wave mixing with pumping by a single diffraction coupled laser beam: Configurations for high spatial resolution"; *Appl Optics* 20:9:1685-1690; 1981.

14. Bjorklund, G.C. "Effects of focussing on third-order non-linear processes in isotropic media"; *IEE J Quantum Electron* QE-11:6:287-296; 1975.

15. Owyoung, A. and Rahn, L.A. "IEEE/OSA Conf. on laser engineering and applications, Digest of CLEA papers; *IEEE J Quantum Electron* QE-15:25D-26D; 1976.

16. Tolles, W.M.; Nibler, J.W.; McDonald, J.R.; and Harvey, A.B. "A review of the theory and application of coherent anti-Stokes Raman spectroscopy (CARS)"; *Appl Spectrosc* 31:4:253-271; 1977.

17. Eckbreth, A.C., and Hall, R.J. "CARS thermometry in a sooting flame"; *Combust and Flame* 36:87-98; 1979.

18. Anderson, H.C., and Hudson, B.S. "Coherent anti-Stokes Raman scattering"; *J Mol Spectrosc* 5:142-201; 1978.

19. Druet, S.A., and Taran, J.P.E. "CARS spectroscopy"; *Progr Quantum Electron* 7:1; 1981.

20. Dewitt, R.N.; Harvey, A.B.; and Tolles, W.M. "Theoretical development of third-order susceptibility as related to coherent anti-Stokes Raman spectroscopy (CARS)"; *Naval Res Lab Rep* NRL-MR-3260; 1976.

21. Yuratich, M.A. "Effects of laser linewidth on CARS"; *Molec Phys* 38:625; 1979.

22. Parameswaran, T. "Program report for CARS (coherent anti-Stokes Raman spectroscopy) project at CANMET"; *Final Rep for DSS* Contract No. 23375-84-7731; October 1985.

23. Teets, R.E. "Accurate convolutions of CARS spectra"; *Optics Letters* 9:226; 1984.

24. Kim. H. "Computer programming in physical chemistry laboratory: Least-squares analysis"; *J Chem Educ* 47:2:120-122; 1970.

25. Eckbreth, A.C.; Dobbs, G.M.; Stufflebeam, J.H.; and Tellex, P.A. "CARS temperature and species measurements in augmented jet engine exhausts"; *AIAA* Pap No. 83-1294; Presented at AISS/ASME/SAE 19th Joint Propulsion Conf; Seattle, WA; June 27-29, 1983.

Table 1 - Characteristics of the holographic grating

Characteristic	Specification
Dimensions	20.32-cm diam
Object focal length	790 mm
Image focal length	820 mm
F/number	4.5
Dispersion	5.3 Å/mm at 475 nm
Dispersion plane	horizontal
Resolution	1.5 cm^{-1} for 50-μm circular image
Efficiency at 475 nm	50% (unpolarized)

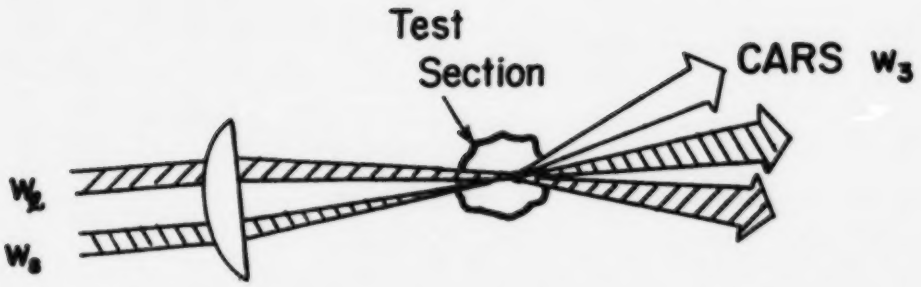


Fig. 1 - Schematic of the generation of a coherent, anti-Stokes Raman signal

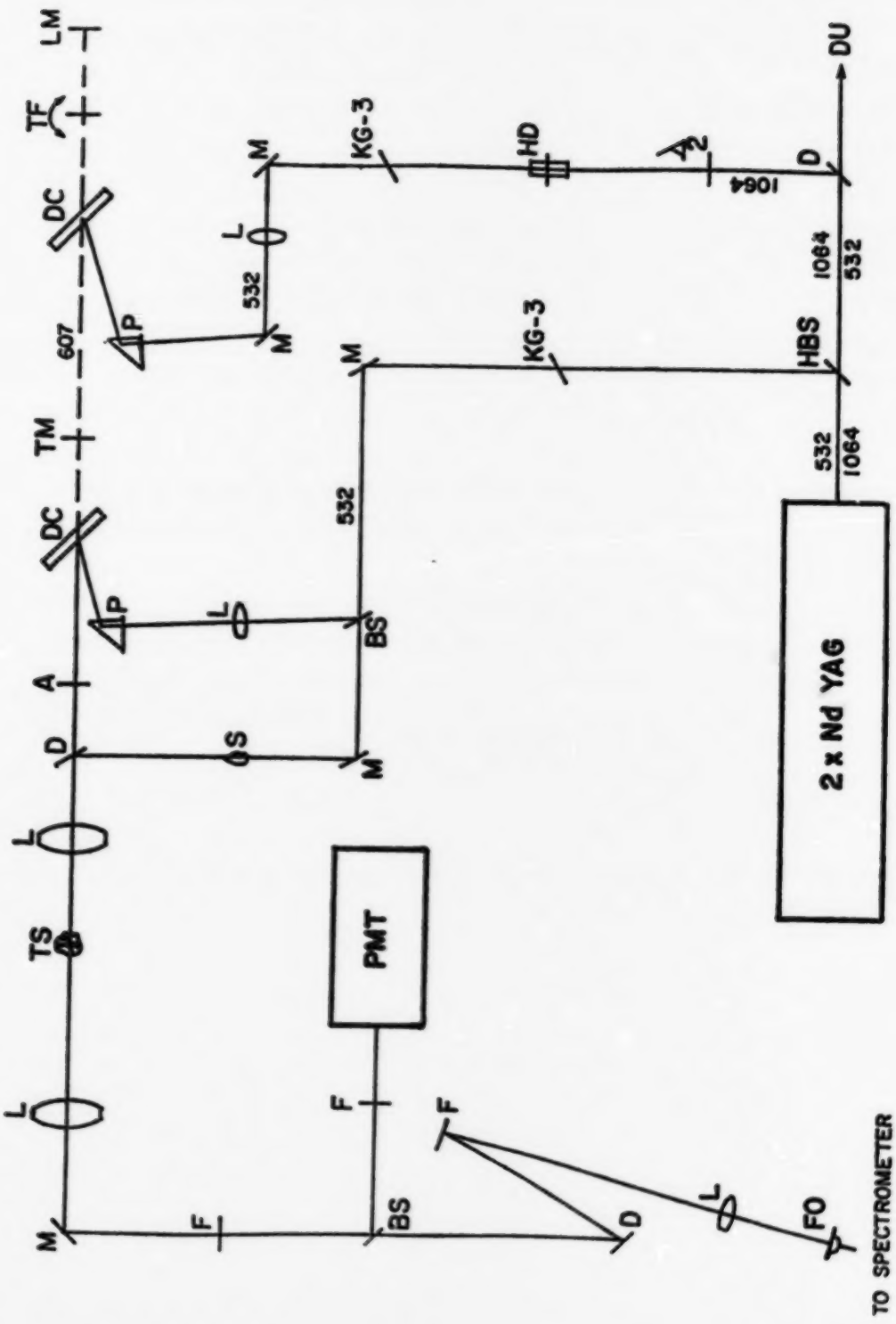


Fig. 2 - Optical arrangement for a CARS experiment

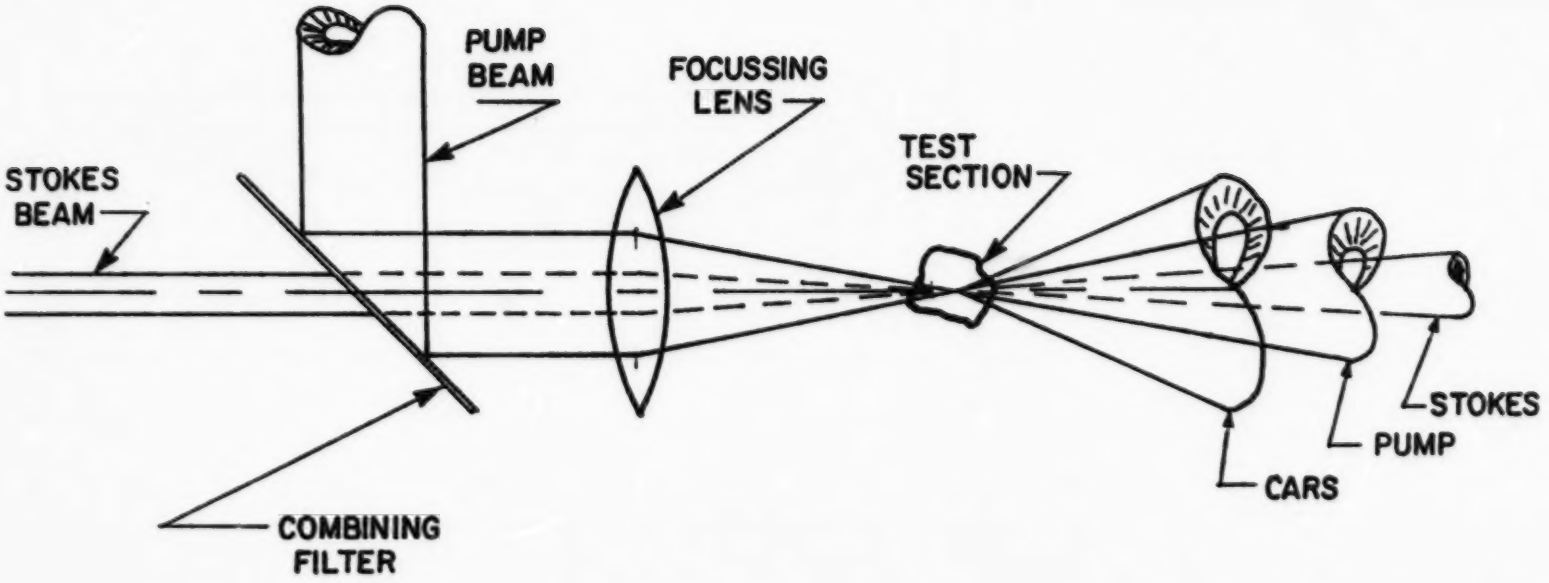
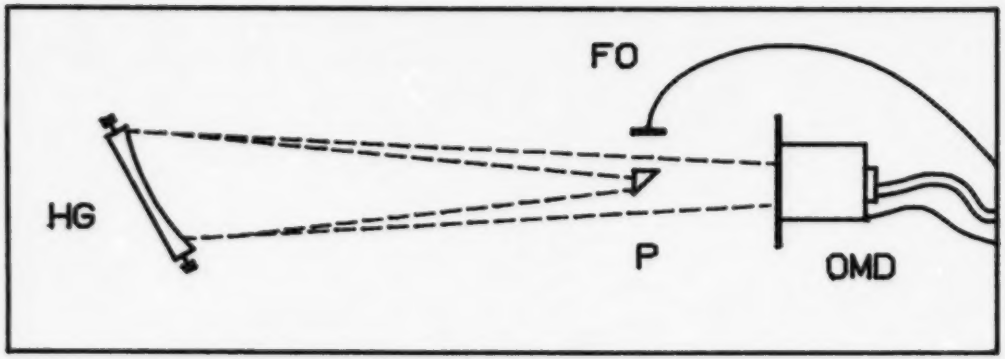
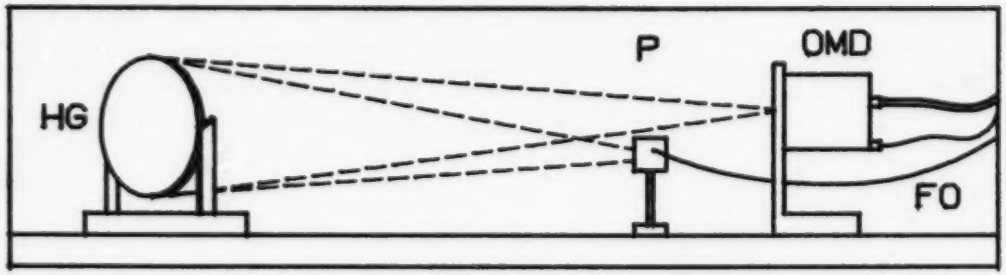


Fig. 3 - Relative positions of the CARS, pump, and Stokes beams



TOP VIEW



SIDE VIEW

OMD - OPTICAL MULTICHANNEL DETECTOR

P - PRISM

FO - FIBER OPTIC

HG - HOLOGRAPHIC GRATING

Fig. 4 - Schematic diagram of the holographic grating spectrometer

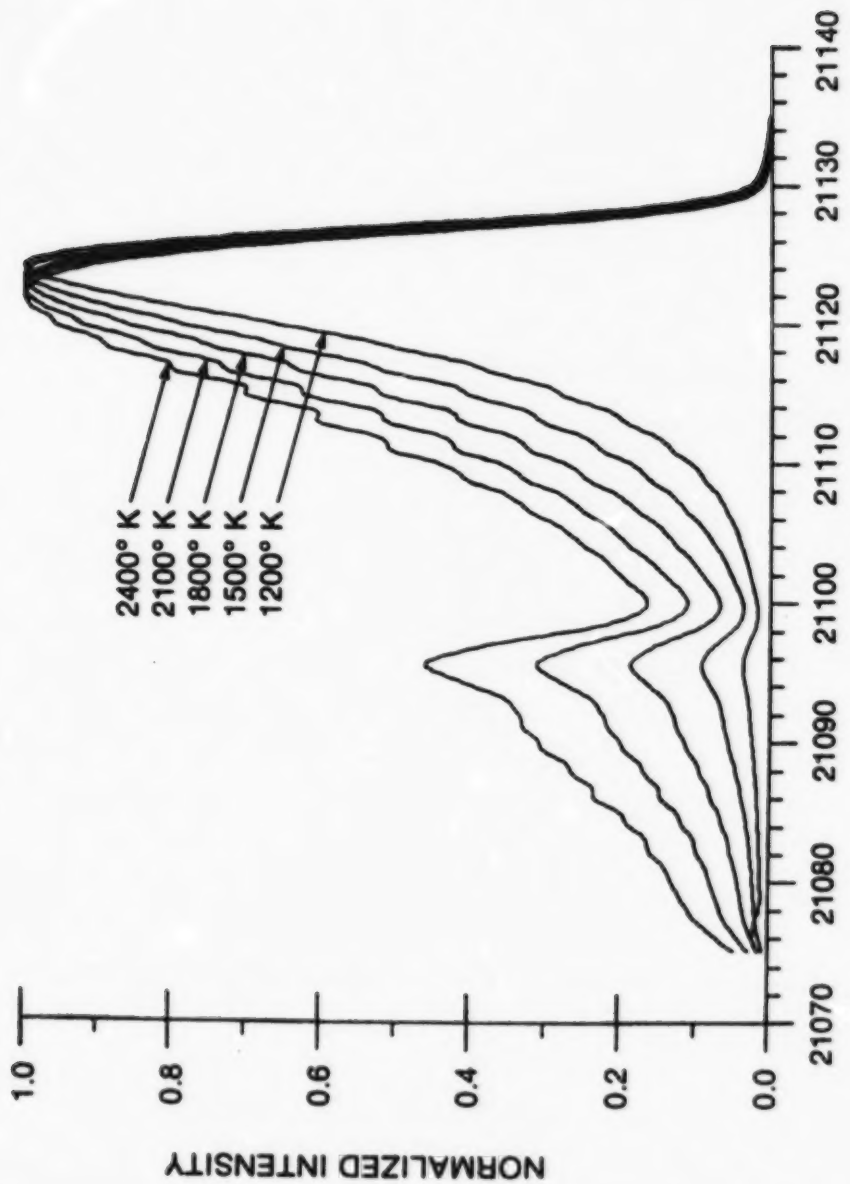


Fig. 5 - Effect of temperature on the CARS spectral profile for Q-branched nitrogen

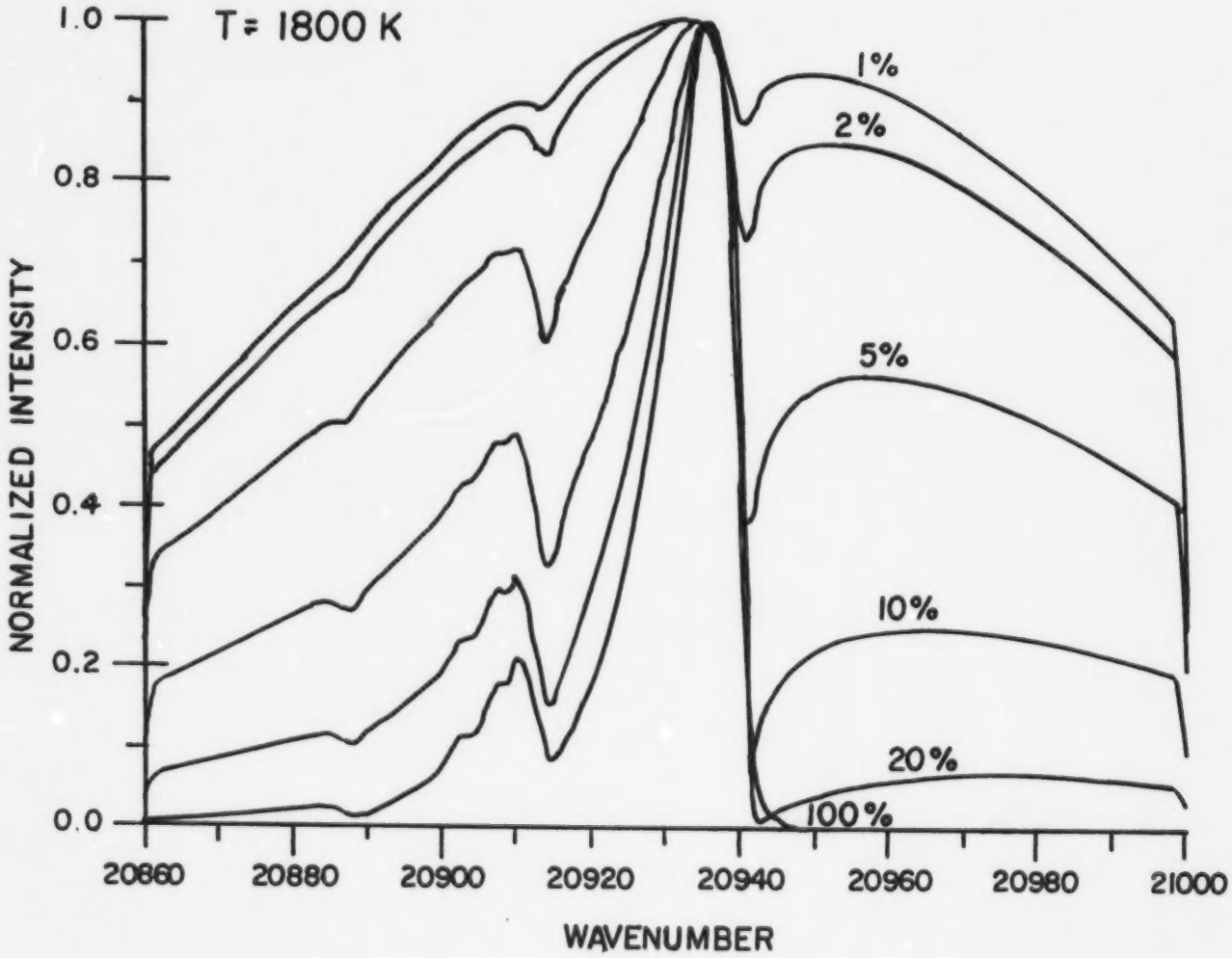


Fig. 6 - Variation of the CO CARS spectrum with concentration

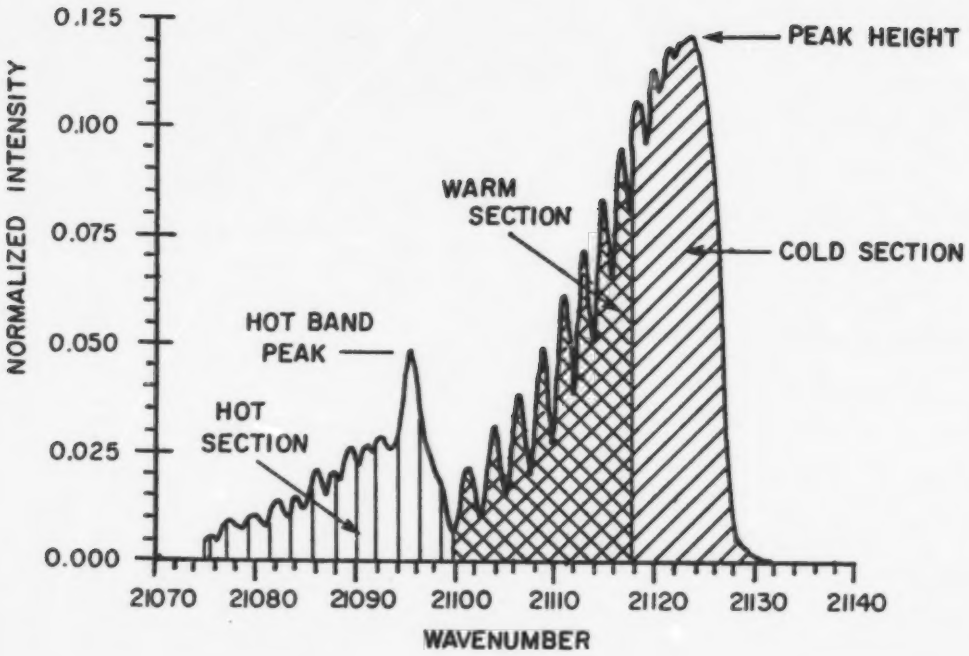


Fig. 7 - Parameters for the fast-fitting algorithms

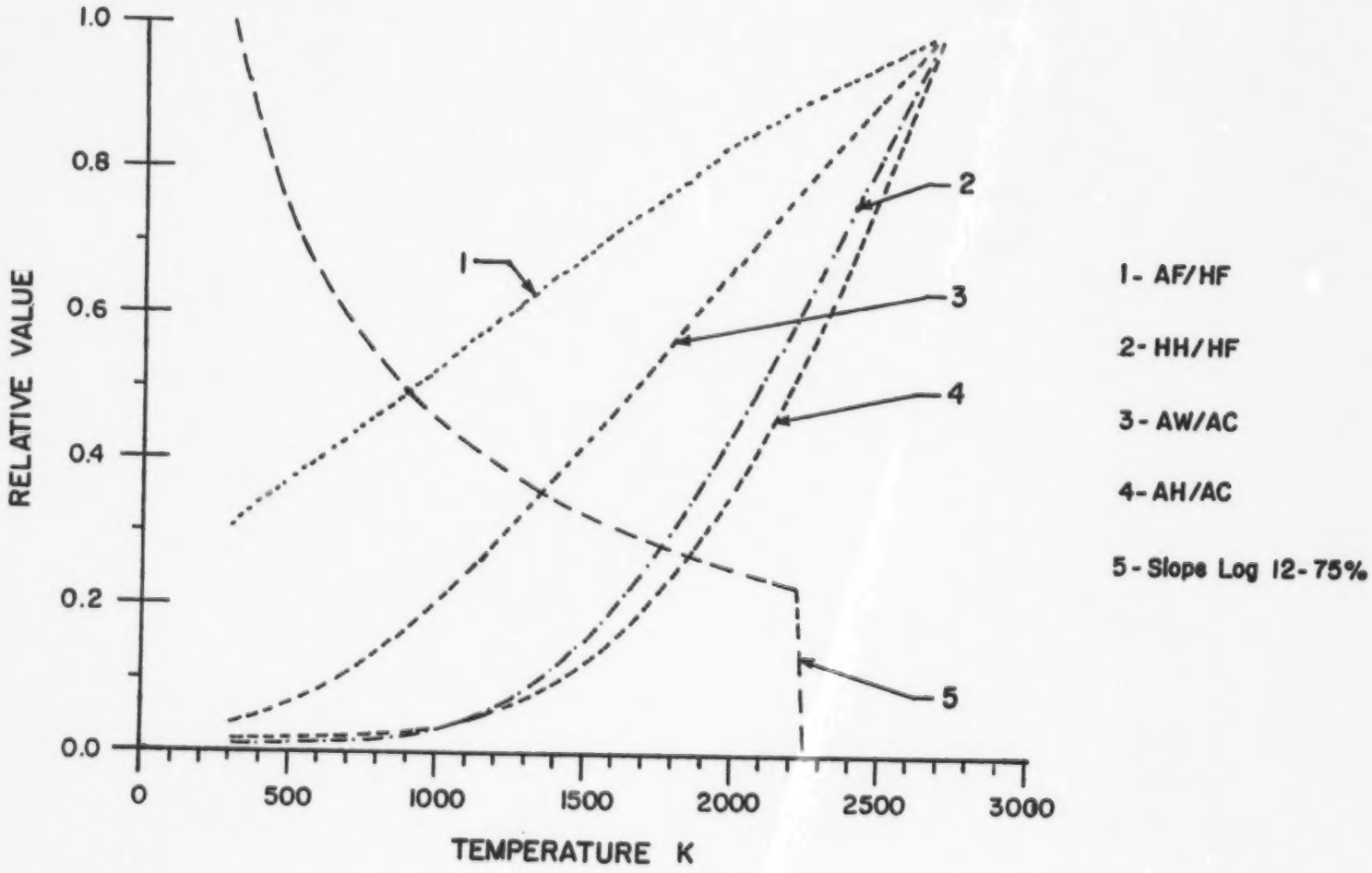


Fig. 8 - Variation of fast-fitting parameters with temperature

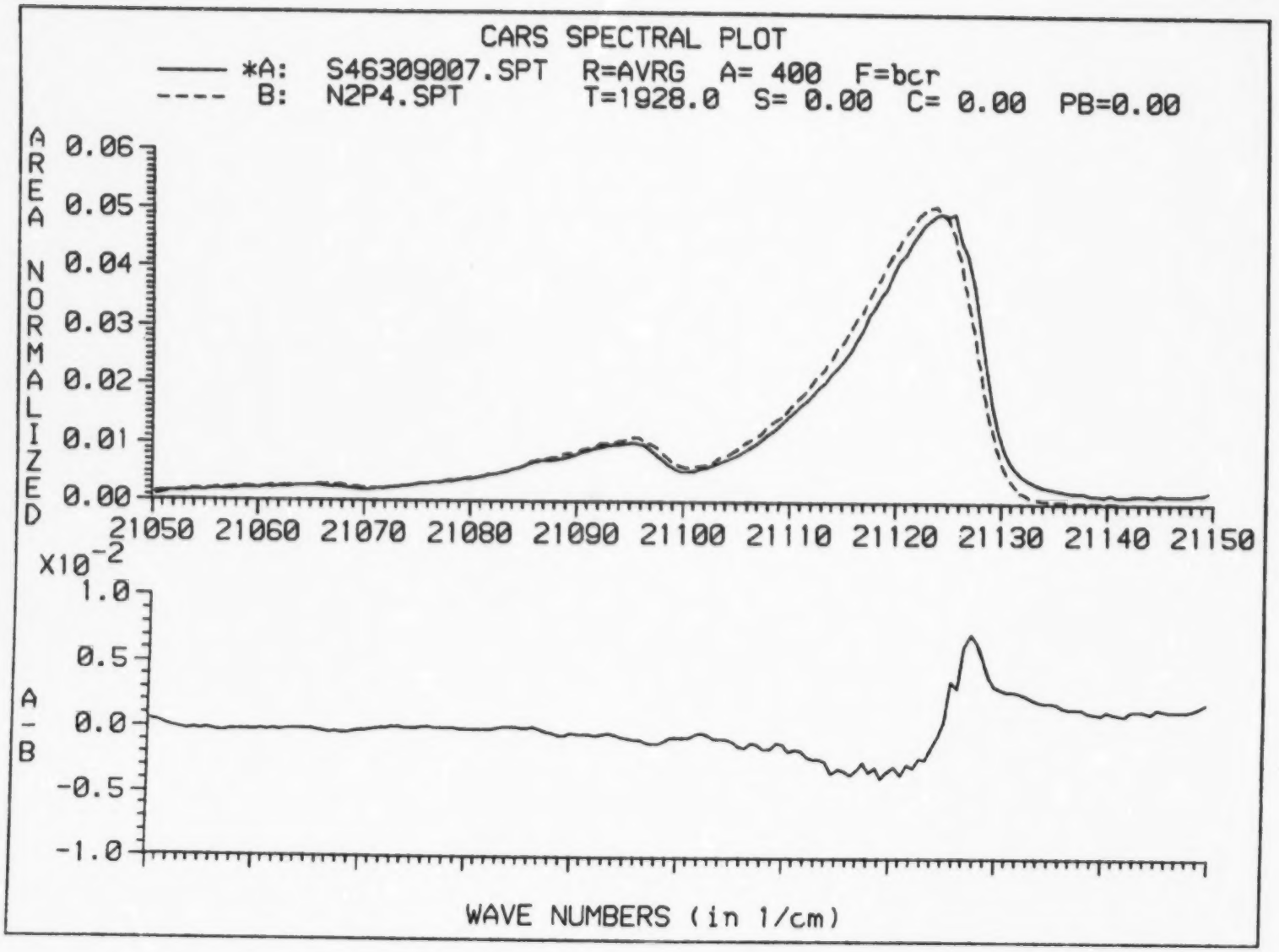


Fig. 9 - Sample figure drawn by the display software